γ-Radiolysis of Isobutyraldehyde at Low Doses. Formation of Propane by Chain Mechanism*

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It was found that the yield of C_3H_8 was very high when liquid isobutyraldehyde was subjected to γ radiolysis at low doses irrespective of dose rate. G(CO) and $G(C_3H_8)$ reached several hundred under optimum conditions. Radical chain mechanism are suggested by scavenging studies.

We have found that the yield of propane produced by γ radiolysis of liquid isobutyraldehyde becomes very high at low doses. High radiation chemical yields at low doses are of essential importance for the utilization of ionizing radiation. High yields of radiolysis products at low doses have been observed in the γ radiolysis of deaerated aqueous solution of carbon dioxide[1-3] and aqueous solution of CF_2HCl[4].

Recently, we also reported radiation-induced chain isomerization of cis-2-butene in benzene solution at low doses[5]. Furthermore, the formation of telomer has been reported in the γ radiolysis of liquid isobutyraldehyde containing unsaturated compounds[6-9]. The γ radiolysis of cyclohexanol solution of isobutyraldehyde have also been reported[10] in connection with the γ-induced isomerization of liquid cyclohexanol.

In this communication we wish to report the results obtained by γ irradiation of liquid isobutyraldehyde and to discuss the reaction mechanism briefly which predominates at low doses.

Guaranteed-grade isobutyraldehyde (Wako Pure Chemicals) was dried over anhydrous potassium sulfate before distillation in the nitrogen atmosphere. Purified aldehyde was degassed and stored in a pyrex bulb. γ-Irradiation was carried out at room temperature using 12-kCi ^{60}Co. Dose rates were 145–12360 rad min^{-1}.

Analysis of gaseous product was made by gaschromatography using 2-m Molecular Sieve 5A column for H_2, CO and CH_4, and 3-m charcoal column for C_3H_6 and C_3H_8 at 50°C and 150°C, respectively.

Dose and dose rate dependence of $G(C_3H_8)$ are shown in Figure 1 and Table 1. $G(C_3H_8)$ increases abruptly to the order of 10^2 at doses of the order of 10^3 and 10^4 rads at low and high dose-rates, respectively. At low dose-rates, the yield of carbon monoxide also becomes high (column I in Table 1), while this is not the case at high dose-rates (column II in Table 1).

In the photolysis of isobutyraldehyde, Kerr and Trotman-Dickenson proposed following primary processes[11]:

$$(CH_3)_2CHCHO^* \begin{cases} \longrightarrow CH_3\cdot + C_2H_4CHO & (1) \\ \longrightarrow C_3H_7\cdot + CHO\cdot & (2) \\ \longrightarrow C_3H_8 + CO & (3) \end{cases}$$

Since the chain reaction breaks by addition of a radical scavenger (DPPH), it may be sufficient to discuss within limits of radicals produced from radiolytic precursors (ions and excited molecules).

Reactions (2) and (3) are assumed to be

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predominant, because of negligible yield of CH_4 which may be produced by reaction (1). C_3H_7 radicals may undergo recombination, disproportionation, and abstraction. Among these reactions, however, recombination can be excluded, because no 2,3-dimethylbutane was detected.

Abstraction of hydrogen atoms from isobutyraldehyde molecules with C_3H_7· occurs presumably at the aldehyde group, because the activation energy is known to be lowest[11].

On the basis of the arguments mentioned above, the results obtained at low doses and at low dose-rates (Curve (A) in Fig. 1) could be accounted for by assuming a radical chain pro-

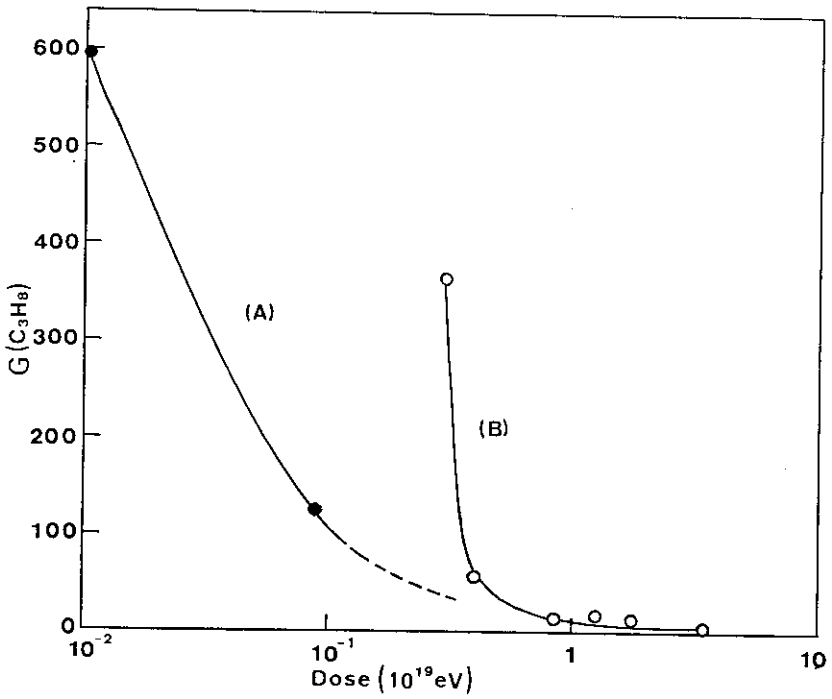

Fig. 1 Dose and dose-rate dependence of $G(C_3H_8)$.
(A) : 145 rad min^{-1}, (B) : 5840–12360 rad min^{-1}

Table 1. Dose and dose-rate dependence of G-values of H_2, CO, C_3H_6 and C_3H_8 in the γ radiolysis of isobutyraldehyde. (I) : G-values at low dose-rate (145 rad min^{-1}),(II) : G-values at high dose-rate (5840–12360 rad min^{-1})

Dose (rad)	G-values							
	H_2		CO		C_3H_6		C_3H_8	
	I	II	I	II	I	II	I	II
1.6×10^3	10.9		1175		0		600	
1.4×10^4	11.9		185		0		130	
4.8×10^4		3.8		11.0		108		370
6.4×10^4		9.2		8.8		40		60
1.4×10^5		3.9		9.5		5.4		16
2.4×10^5		2.3		7.4		2.4		22
4.0×10^5		4.0		7.4		0.4		16
5.6×10^5		4.3		7.4		0.5		6

Table 2. Effect of radical scavenger on the yields of CO and C_3H_8 in the γ radiolysis of isobutyraldehyde at low dose [(1.3-1.4) x 10^3 rad] and at low dose-rate (145 rad min^{-1})

	G-values	
	CO	C_3H_8
Pure	1175	612
DPPH ($\sim 10^{-2}$ MOL/DM^3)	12.5	7.5

cess represented by reaction (4) and (5):

$$C_3H_7\cdot + (CH_3)_2CHCHO \longrightarrow C_3H_8 + (CH_3)_2\dot{C}HCO \quad (4)$$

$$(CH_3)_2\dot{C}HCO \longrightarrow C_3H_7 + CO \quad (5)$$

Effects of a radical scavenger (DPPH) on these product yields, shown in Table 2, support above process. At higher dose regions, the yield of C_3H_6 is expected to increase by additional reactions of $G_3H_7\cdot$ radicals, such as disproportionation.

On the basis of the results reported by Stoops and Furrow[6] that the γ-induced chain reaction is brought about between C_3H_6 and isobutyraldehyde to give telomer, yields of CO and C_3H_8 may decrease by the accumulation of lower telomer [reaction (7)].

$$(CH_3)_2\dot{C}HCO + CH_3CH{=}CH_2 \longrightarrow CH_3\dot{C}HCH_2 \quad (6)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad COCH(CH_3)_2$$

$$CH_3\dot{C}HCH_2$$
$$\quad |$$
$$COCH(CH_3)_2 \quad + (CH_3)_2CHCHO \longrightarrow$$

$$\{(CH_3)_2CH\}_2CO \;+\; (CH_2)_2\dot{C}HCO \quad (7)$$

Production of C_3H_6 has been found to increase rapidly from about 280°C by examining the effect of reaction temperature in the photolysis of isobutyraldehyde[11]. Reaction (8)–(10) were suggested to elucidate the above described result, though the activation energy of the abstraction of hydrogen atoms from methyl group in isobutyraldehyde molecules is little higher than that from aldehyde group.

$$C_3H_7\cdot + (CH_3)_2CHCHO \longrightarrow C_3H_8 + \dot{C}H_2(CH_3)CHCHO \quad (8)$$

$$\dot{C}H_2(CH_3)CHCHO \longrightarrow C_3H_6 + HCO \quad (9)$$

$$HCO + (CH_3)_2CHCHO \longrightarrow H_2CO + \dot{C}H_2(CH_3)CHCHO \quad (10)$$

Since the G-values of C_3H_8 and C_3H_6 in low dose irradiation with higher dose-rate, are 370 and 108 respectively, it's satisfactory to consider Reaction (8)–(10) as the mechanism assumed by the dose-rate effect involving temperature effect. Reaction (10) might be postulated because of the marked deficiency of hydrogen in the products as is shown in Table 1.

At high dose irradiation with higher dose-rates, the yield of C_3-fraction may decrease by the formation of higher telomers according to Reaction (11). [Curve (B) in Fig. 1].

$$\dot{R}CO \xrightarrow{n\cdot C_3H_6} RCO{-}\{{-}CH_3CHCH_2\}_n + \dot{R}CO \quad (11)$$

In fact, we could observe a small amount of polymer remaining on the glass wall of the irradiation cell..

In the present communication only the qualitative explanation was given to the reason why the chain mechanism breaks at high-doses independently of dose-rates; these results may give important insight into low-dose radiolysis studies. Extensive studies of this system are in progress.

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